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Dynamics of a charged simple fluid with exponential memory and two relaxation times

J. E. Flores-Mena and J. L. Carrillo
Instituto de Física de la Universidad Autónoma de Puebla, Apartado Postal J-48, Puebla 72570, Puebla, Mexico

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The memory function formalism is applied to the study of charge fluctuations in a symmetric simple fluid. We assume the ions interact through the Rammanathan-Friedman potential. We calculate the distribution function using the hypernetted-chain approximation and use an exponential form, depending on two relaxation times, for the second-order memory function. Following this procedure, two algebraic equations for the relaxation times are obtained. These can be solved using the fourth- and sixth-order frequency momenta, yielding expressions for the relaxation times in terms of the characteristic parameters of the system. This approach allows the analysis of the dynamical structure factor and the dynamical behavior of the charge fluctuations. A comparison of these results with some recently reported in which the distribution function is calculated via mean spherical approximation theory, shows clearly the limitations of mean-field formalisms to describe the dynamics of charged fluids.

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I. INTRODUCTION

The dynamics of charged fluids is presently a topic of intensive research activity. In the last decade, there has been significant progress in understanding and describing the static structural properties of these systems. However, with respect to the dynamical behavior, some fundamental questions still remain. The answers to these questions are relevant not only in the investigation of charged fluids, but in general, for strongly correlated particle systems in condensed-matter physics. In charged fluids, the screening and the fluctuations of the charge density are features of the system that determine the dynamical response to an external field. When the system is in equilibrium, the long range of the Coulomb potential produces an effective screening of the electric fields and the charge fluctuations become negligible [1,2]. If the system is driven out of equilibrium by an external field, the screening of electrostatic fields is less effective, the charge fluctuations become relevant, and the charge fluctuations determine the features of the dielectric response of the system.

The dynamical behavior of charged fluids has been studied experimentally by inelastic neutron scattering [3] and x-ray and light scattering [4]. Some theoretical procedures and techniques have been developed in the search to describe the dynamics of these systems. Most of these theoretical approaches are based on mean-field approximations [5] or on the memory function formalism [6–9]. However, these approaches cannot be extrapolated into the hydrodynamic regime. Computer simulations are nowadays one of the most powerful tools in the investigation of complex fluids [10–12]. In order to establish a theoretical model, comparisons between the results given by theories and numerical simulations can be used to improve both of them.

Due to their wide variety of applications and to the important basic physical problems involved, molten salts have been studied extensively during the last decades [13]. The understanding of these Coulombic systems has great relevance for several branches of the natural sciences. Although our treatment can, in principle, be applied to study some other simple charged fluids, in this paper we focus our attention in the analysis of symmetric molten salts.

Most of the theoretical descriptions of charged fluids are based on the mean spherical approximation (MSA) [9]. This approach provides analytical expressions for the relevant quantities. However, MSA is a theory for hard-sphere fluids, consequently it neglects some important features, which for the description of molten salts, must be considered. There have been some other theoretical approaches that assume more realistic potentials than the mean-field potential implied in the MSA [14]. Example of these are the soft and the polarizable ion models. These models containing more realistic potentials provide better accuracy in the description of the dynamics of molten salts. However, their range of practical applicability is still quite restricted and the strengths and positions of the collective modes, as predicted by them, exhibit certain error. Nevertheless, these models allow some insight on the dynamics of simple and complex liquids [14]. In this paper we used the Mori-Zwanzig memory function formalism as well as the hypernetted chain (HNC) approximation to obtain simple analytical expressions for the charge-charge fluctuations. The theoretical framework is discussed in the next section. We focus particularly our attention on the relaxation processes of charge fluctuations; in this analysis we explore an exponential second-order memory function, which depends on two relaxation times. This is discussed in the third section. Finally, we make a detailed comparison with results we previously obtained [15] by the use of MSA, and with other pertinent results. This makes evident the limitations of mean-field theories in the description of dynamical properties of charged fluids.

II. THEORETICAL FRAMEWORK

In the primitive model for a molten salt, the set of N ions are modeled by charged hard spheres. For this discontinuous potential, it is not possible to use a frequency momenta expansion to calculate the charge-charge fluctuations [11]. To avoid this difficulty and in order to obtain analytical expressions for the even frequency momenta, we adopt a Rammanathan-Friedman potential with the following representation [16]:

$$v_{\alpha\beta}(r)=\frac{e^2}{a}\left[\frac{1}{n}\left(\frac{a}{r}\right)^n+z_\alpha z_\beta\left(\frac{a}{r}\right)\right]. \tag{1}$$

In the limit $n\rightarrow\infty$, the hard-sphere approach is recovered. We use Eq. (1) to calculate the pair-correlation function $g_{\alpha\beta}(r)$ within the HNC approximation. For comparisons, we also consider the primitive model for a molten salt and deal with the hard-sphere term using Perram's algorithm [17] to calculate the electric contribution of the distribution function applying the zone expansion within MSA [18].

We use the projection-operator formalism to describe the dynamics of a molten salt. After Gianquinta *et al.* [8], we select the following microscopic set of conserved variables: the density of mass $\rho_k(t)$, the longitudinal density current of mass $J_k^M(t)$, the density of charge $Q_k(t)$, the longitudinal density current of charge $J_k^Q(t)$, and the temperature $T_k(t)$ [19]. These quantities are defined as follows

$$\rho_k(t)=\sum_{j=1}^{N} m_j e^{i\mathbf{k}\cdot\mathbf{r}_j(t)}, \tag{2}$$

$$J_k^M(t)=\sum_{j=1}^{N} m_j v_j^l(t) e^{i\mathbf{k}\cdot\mathbf{r}_j(t)}, \tag{3}$$

$$Q_k(t)=\sum_{j=1}^{N} q_j e^{i\mathbf{k}\cdot\mathbf{r}_j(t)}, \tag{4}$$

$$J_k^Q(t)=\sum_{j=1}^{N} q_j v_j^l(t) e^{i\mathbf{k}\cdot\mathbf{r}_j(t)}, \tag{5}$$

$$T_k(t)=\frac{1}{C_v(k)}[E_k(t)-O_1(k)\rho_k(t)-O_2(k)Q_k(t)], \tag{6}$$

where

$$O_1(k)=\frac{\langle E_k\rho_{-k}\rangle\langle Q_kQ_{-k}\rangle-\langle E_kQ_{-k}\rangle\langle Q_k\rho_{-k}\rangle}{\langle \rho_k\rho_{-k}\rangle\langle Q_kQ_{-k}\rangle-\langle \rho_kQ_{-k}\rangle\langle Q_k\rho_{-k}\rangle}, \tag{7}$$

$$O_2(k)=\frac{\langle E_kQ_{-k}\rangle\langle \rho_k\rho_{-k}\rangle-\langle E_k\rho_{-k}\rangle\langle \rho_kQ_{-k}\rangle}{\langle \rho_k\rho_{-k}\rangle\langle Q_kQ_{-k}\rangle-\langle \rho_kQ_{-k}\rangle\langle Q_k\rho_{-k}\rangle}. \tag{8}$$

$E_k(t)$ is the energy density expressed in terms of the interionic potential V_{ij}, and $C_v(k)$ is the heat capacity at constant volume. These quantities are, respectively, given by

$$E_k(t)=\sum_{i=1}^{N}\left[\frac{m_i\mathbf{v}_i^2(t)}{2}+\frac{1}{2}\sum_{j\neq i}^{N}V_{ij}(r_{ij})\right]e^{i\mathbf{k}\cdot\mathbf{r}_i(t)} \tag{9}$$

and

$$C_v(k)=\frac{K_BT^2}{\langle T_k^2\rangle}. \tag{10}$$

These dynamical variables may be considered as the components of the vector

$$\mathbf{A}_k(t)=\begin{pmatrix}\rho_k(t)\\ J_k^M(t)\\ T_k(t)\\ Q_k(t)\\ J_k^Q(t)\end{pmatrix}. \tag{11}$$

The equation of motion $\mathbf{A}_k(t)$ is the following:

$$\frac{d\mathbf{A}_k(t)}{dt}-i\mathbf{\Omega}_k\mathbf{A}_k(t)+\int_0^t\mathbf{M}_k(t-s)\mathbf{A}_k(s)ds=\mathbf{R}_k(t), \tag{12}$$

where $\mathbf{\Omega}_k$ is the frequency matrix, $\mathbf{M}_k(t)$ is the memory function matrix, and $\mathbf{R}_k(t)$ is the random force vector [20]. From the above equation-of-motion and the Fourier-Laplace transform definition, the correlation function matrix $\tilde{\mathbf{C}}_{AA}(k,z)$ can be expressed in the form

$$[z\mathbf{I}-i\mathbf{\Omega}_k+\tilde{\mathbf{M}}(k,z)]\tilde{\mathbf{C}}_{AA}(k,z)=\mathbf{C}_{AA}(k,0). \tag{13}$$

The relationship between the susceptibility matrix $\tilde{\boldsymbol{\chi}}_{AA}(k,z)$ and $\tilde{\mathbf{C}}_{AA}(k,z)$ is a well-known result of the linear-response theory

$$\tilde{\boldsymbol{\chi}}_{AA}(k,z)=\frac{1}{k_BT}[\mathbf{C}_{AA}(k,0)+iz\tilde{\mathbf{C}}_{AA}(k,z)]. \tag{14}$$

The explicit representation of the matrices of this relation can be considerably simplified if one applies usual symmetry operations [21]. As an example, for a symmetric molten salt, if in addition one considers the charge conjugation symmetry operation the frequency matrix can be cast into the form

$$i\mathbf{\Omega}_k=\begin{pmatrix} 0 & ik & 0 & 0 & 0\\ \dfrac{ik\rho k_BT}{\langle\rho_k\rho_{-k}\rangle} & 0 & \dfrac{\left\langle \dfrac{dJ_k^M}{dt}T_{-k}\right\rangle}{\langle T_kT_{-k}\rangle} & 0 & 0\\ 0 & -\dfrac{\left\langle T_k\dfrac{dJ_{-k}^M}{dt}\right\rangle}{\rho k_BT} & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & ik\\ 0 & 0 & 0 & \dfrac{ik\omega_p^2k_BT}{4\pi\langle Q_kQ_{-k}\rangle} & 0 \end{pmatrix}. \tag{15}$$

In this way, the quantities ρ_k, J_k^M, and T_k are decoupled in Q_k and J_k^Q. From the expression (13) we obtain the various correlation functions.

The dynamic charge-charge self-correlation $\tilde{S}_{QQ}(k,z)$ is given by

$$\tilde{S}_{QQ}(k,z)=\langle Q_k Q_{-k}\rangle \times \left(z+\frac{k^2\langle J_k^Q J_{-k}^Q\rangle/\langle Q_k Q_{-k}\rangle}{z+\tilde{R}_{55}(k,z)/\langle J_k^Q J_{-k}^Q\rangle}\right)^{-1}, \tag{16}$$

where $\tilde{R}_{55}(k,z)$ is the second-order memory in its partial fraction series representation for the charge-charge self-correlation. Obviously, an explicit expression for this quantity cannot be obtained from this formalism.

The following two expressions are well known and useful in the context of linear-response theory. The first one is the relationship between the charge-charge self-correlation $\tilde{S}_{QQ}(k,z)$ and the dynamic charge-charge structure factor,

$$S_{QQ}(k,\omega)=\frac{1}{\pi}\mathrm{Re}\,\tilde{S}_{QQ}(k,z). \tag{17}$$

The second is the relation between the statistical susceptibility $\chi_{QQ}(k,\omega)$ and the longitudinal dielectric function $\epsilon(k,\omega)$:

$$\frac{1}{\epsilon(k,\omega)}=1+\frac{4\pi q^2}{k^2}\chi_{QQ}(k,\omega). \tag{18}$$

We wish to calculate the dynamic structure factor associated to the charge-charge fluctuations $S_{QQ}(k,\omega)$. Since, this theoretical framework is unable to provide an explicit form for the memory function, we propose an heuristic expression for the memory function $\tilde{R}_{55}(k,z)$. In order to explain this approximation, let us consider the relation

$$\frac{\tilde{R}_{55}(k,z)}{\langle J_k^Q J_{-k}^Q\rangle}=\frac{R_{55}(k,0)}{\langle J_k^Q J_{-k}^Q\rangle}\tilde{N}(k,z), \tag{19}$$

where $\tilde{N}(k,z)=\tilde{R}_{55}(k,z)/R_{55}(k,0)$ is the normalized memory function. By using the projection-operator formalism and the symmetry properties we can write,

$$\frac{R_{55}(k,0)}{\langle J_k^Q J_{-k}^Q\rangle}=\omega_{1l}^2-\frac{\omega_0^2(ze)^2\rho}{S_{QQ}(k)}, \tag{20}$$

where the frequency ω_{1l}^2 is given by the general Abramo expression [22]. This expression is valid for continuous potentials. We have used here the soft sphere potential, Eq. (1), with $n=9$ and $a=2.34$ Å [20].

For a symmetric molten salt the expression for ω_{1l}^2 acquires the form

$$\left(\frac{\omega_{1l}}{\omega_p}\right)^2=3\left(\frac{\omega_0}{\omega_p}\right)^2+\frac{2}{3}+\frac{1}{16\pi}\sum_\alpha\sum_\beta z_\alpha z_\beta\left\{\frac{1}{na}\int g_{\alpha\beta}(r)\times(1-\cos kz)\frac{d^2}{dz^2}\left(\frac{a}{r}\right)^n d\vec{r}+z_\alpha z_\beta\int[g_{\alpha\beta}(r)-1]\times(1-\cos kz)\frac{d^2}{dz^2}\left(\frac{1}{r}\right)d\vec{r}\right\}+\frac{1}{12\pi an}\int g_{12}(r)\times\nabla^2\left(\frac{a}{r}\right)d\vec{r}. \tag{21}$$

In Eqs. (20) and (21), the frequency ω_0 is given by $\omega_0=(zk)^2k_BT/m$ and in Eq. (20), $S_{QQ}(k)$ is the static charge-charge fluctuation that is directly related to the static structure factor $S_{zz}(k)$,

$$S_{QQ}(k)=(ze)^2\rho S_{zz}(k). \tag{22}$$

The normalized Fourier-Laplace transformed memory function $\tilde{N}(k,z)$ has the form

$$\tilde{N}(k,z)=\frac{m(k)}{\tau_1^{-1}+z}+\frac{n(k)}{\tau_2^{-1}+z}, \tag{23}$$

that was obtained assuming an exponential approximation. Through this expression we wish to incorporate in our theoretical description the possibility of exploring the influence on the response function of relaxation processes with different relaxation times. We shall associate τ_{01} and τ_{02} with precesses with short and long relaxation times, respectively.

III. APPROXIMATION WITH TWO RELAXATION TIMES

In a previous work, we have reported an analysis of the charge-charge fluctuations in a simple charged fluid [15], considering an exponential memory function depending on a single relaxation time. This is a suitable memory approximation for the long-times regime [23]. In that work we have found that the results for the charge-charge fluctuations obtained within that scheme are qualitatively good for the moderately high-frequency regime. However, in that approach there exists an inconsistency in the calculation of the static properties of the system, since on the one hand, the distribution function is obtained via MSA considering a hard-sphere potential, and on the other hand, the Abramo expression for the frequency ω_{1l}^2 is obtained through expression (21), using a soft-sphere potential, Eq. (1). In order to correct this inconsistency, in this paper we calculate the radial distribution function, by means of the HNC approximation [24] and the Abramo expression for the frequency ω_{1l}^2, both within the same potential model, expression (1). It is worthy to comment that the results discussed in Ref. [15], in the low-frequency regime of the charge-charge fluctuations spectrum, in general, exhibit a poor agreement with the results obtained by molecular dynamics (MD). This deficient description can be associated with the intrinsic limitations of MSA. Under dynamical conditions one may expect that some information beyond a mean-field interaction would improve our results. Thus, it is clear that mean-field theories are not capable to describe properly the physics of charged fluids in the hydrodynamic limit. More detailed information about nearestneighbors interactions and associated fluctuations is needed to describe the system collective modes and its corresponding dynamic response.

As mentioned above, it has been shown that the exponential memory depending on one relaxation time provides a suitable description for the charge-charge fluctuations in the long-times regime [23]. In order to improve the description in the hydrodynamic limit, here we explore an exponential memory depending on two relaxation times. This expression (23) is a generalization of the usual expression depending on one single relaxation time, $\tilde{N}(k,z)=(\tau^{-1}+z)^{-1}$. In the short-times regime a Gaussian form for the second-order memory provides better results than an exponential one, but an exponential form has the advantage of yielding an analytical expression for its Fourier-Laplace transform. Hence, in our studies, we calculate the static properties, i.e., the pair-correlation function and second-order frequency momentum, using a charged soft-sphere potential, and an exponential form for the second-order memory, depending on two relaxation times corresponding to the short- and long-times regimes, respectively. We analyze in particular the dynamics of a symmetric two-component molten salt specified by the following parameters [11]: molarity $M=23.866$, temperature $T=1267$ K, coefficient of soft sphere $n=9$, and ionic radius $a=2.34$ Å .

The projection operator formalism itself is not capable to provide an expression for the second-order memory, consequently we explore the following alternative expression:

$$N(k,t)=me^{-t/\tau_1}+ne^{-t/\tau_2}, \tag{24}$$

We assume that τ_1 and τ_2 correspond to characteristic relaxation times in the short- and long-times regimes, respectively. Due to the definition of the memory function, which is a normalized quantity [see expression (19)] the amplitudes m and n satisfy $m+n=1$. Notice that we have suppressed the wave vector dependence of the amplitudes n and m. To determine this dependence we would need an additional condition. We take this to be the seventh-order momentum, which would provide an algebraic equation with a higher-order polynomial. The amplitudes n and m, in general, depend on the wave vector k. We assume here a certain dependence and use these amplitudes together with the restriction $n+m=1$ to construct a trial function for the second-order memory function.

From the inverse Fourier-Laplace transform of expression (24), we obtain for the correlation of the charge-charge fluctuations

$$F_{QQ}(k,t)=\lambda_1 e^{-t/\tau_2}\mathcal{L}^{-1}\left\{\frac{z^3+N_1z^2+N_2z+N_3}{z^4+D_1z^3+D_2z^2+D_3z+D_4}\right\}, \tag{25}$$

where

$$N_1=\tau_1^{-1}-2\tau_2^{-1}, \tag{26}$$

$$N_2=\tau_2^{-2}-\tau_1^{-1}\tau_2^{-1}+b_1, \tag{27}$$

$$N_3=b_1n(\tau_1^{-1}-\tau_2^{-1}), \tag{28}$$

$$D_1=\tau_1^{-1}-3\tau_2^{-1}, \tag{29}$$

$$D_2=3\tau_2^{-2}-2\tau_1^{-1}\tau_2^{-1}+b_1+k^2\lambda_2, \tag{30}$$

$$D_3=(\tau_1^{-1}-\tau_2^{-1})(\tau_2^{-2}+k^2\lambda_2+b_1n)-b_1\tau_2^{-1}, \tag{31}$$

$$D_4=-b_1n\tau_2^{-1}(\tau_1^{-1}-\tau_2^{-1}), \tag{32}$$

and

$$\lambda_1=\langle Q_kQ_{-k}\rangle, \tag{33}$$

$$\lambda_2=\langle J_k^QJ_{-k}^Q\rangle/\langle Q_kQ_{-k}\rangle, \tag{34}$$

$$b_1=R_{55}(k,0)/\langle J_k^QJ_{-k}^Q\rangle. \tag{35}$$

To obtain the complete inverse Fourier-Laplace transform from Eq. (25), it is necessary to know the roots of the following fourth-degree algebraic equation:

$$z^4+D_1z^3+D_2z^2+D_3z+D_4=0. \tag{36}$$

This equation can be solved, in principle, in terms of radicals involving a hard-handling algebra work, alternatively, here we find an approximate solution. Notice that when $n\to 0$ the fourth-degree equation can be written in the form $zP_3(z)=0$, i.e., a third-degree polynomial. Thus, in this limit the root z_0 of Eq. (36) can be expressed in the form

$$z_0=a_0n+b_0n^2. \tag{37}$$

Using this in the fourth-degree equation and comparing the coefficients of equal powers of z, we obtain

$$a_0=\frac{b_1\tau_2^{-1}(\tau_1^{-1}-\tau_2^{-1})}{(\tau_1^{-1}-\tau_2^{-1})(\tau_2^{-2}+k^2\lambda_2)-b_1\tau_2^{-1}} \tag{38}$$

and

$$b_0=-\frac{b_1^2\tau_2^{-1}(\tau_1^{-1}-\tau_2^{-1})^2[2\tau_2^{-3}-\tau_1^{-1}\tau_2^{-2}+k^2\lambda_2\tau_1^{-1}]}{[(\tau_1^{-1}-\tau_2^{-1})(\tau_2^{-2}+k^2\lambda_2)-b_1\tau_2^{-1}]^3}. \tag{39}$$

The partial fractions representation of the Fourier-Laplace transform of Eq. (25) is given by

$$F_{QQ}(k,t)=\lambda_1e^{-t/\tau_2}[A_0e^{-z_0t}+Aae^{-z_1t}+Abe^{-z_2t}+Ace^{-z_3t}], \tag{40}$$

where z_1, z_2, and z_3, are the roots of the third-degree equation

$$z^3+D_{01}z^2+D_{02}z+D_{03}=0. \tag{41}$$

The relations for the coefficients D_{01}, D_{02}, D_{03}, and D_s are given by expressions (29)–(32), in the following form:

$$D_{01}=D_1+z_0, \tag{42}$$

$$D_{02}=z_0(D_1+z_0)+D_2, \tag{43}$$

$$D_{03}=-D_4/z_0. \tag{44}$$

The coefficients of exponential terms are given by

$$a=\frac{(z_1^2+N_{01}z_1+N_{02})(z_2-z_3)}{\Delta S}, \tag{45}$$

$$b=\frac{(z_2^2+N_{01}z_2+N_{02})(z_3-z_1)}{\Delta S}, \tag{46}$$

$$c=\frac{(z_3^2+N_{01}z_3+N_{02})(z_1-z_2)}{\Delta S} \tag{47}$$

with

$$\Delta S=z_1^2(z_3-z_2)+z_2^2(z_1-z_3)+z_3^2(z_2-z_1) \tag{48}$$

and

$$N_{01}=B/A, \tag{49}$$

$$N_{02}=C/A. \tag{50}$$

The parameters A_0, A, B, and C, are given by

$$A_0=\frac{z_0^3+N_1z_0^2+N_2z_0+N_3}{z_0^3+z_0^2D_{01}+z_0D_{02}+D_{03}}, \tag{51}$$

$$A=\frac{z_0^2(D_{01}-N_1)+z_0(D_{02}-N_2)+(D_{03}-N_3)}{z_0^3+z_0^2D_{01}+z_0D_{02}+D_{03}}, \tag{52}$$

$$B=\frac{z_0^2(D_{02}-N_2)+z_0(D_{03}+N_1D_{02}-N_2D_{01}-N_3)+(N_1D_{03}-N_3D_{01})}{z_0^3+z_0^2D_{01}+z_0D_{02}+D_{03}}, \tag{53}$$

$$C=\frac{z_0^2(D_{03}-N_3)+z_0(N_1D_{03}-N_3D_{01})+(D_{03}N_2-D_{02}N_3)}{z_0^3+z_0^2D_{01}+z_0D_{02}+D_{03}}. \tag{54}$$

The charge-charge fluctuations given by Eq. (40) in terms of the quantities A_0, A, a, b, c, z_0, z_1, z_2, and z_3 can be written in terms of the relaxation times τ_1 and τ_2. However, these relaxation times are undetermined yet. We wish to derive some expressions for the relaxation times in terms of the characteristic parameters of the system. To do this we use the conditions given by the frequency momenta [20]. The information of the first four frequency momenta is already contained in Eq. (40) through the partial fractions representation for the self-correlation (16). Thus, we need to make use of higher-order momenta. From the fifth-order momentum we have

$$f_1\tau_{01}^{-1}+f_2\tau_{01}^{-1}\tau_{02}^{-2}+f_3\tau_{01}^{-2}\tau_{02}^{-1}+f_4\tau_{02}^{-1}=0 \tag{55}$$

and from the sixth-order momentum

$$g_1\tau_{01}^{-1}\tau_{02}^{-3}+g_2\tau_{01}^{-2}\tau_{02}^{-2}+g_3\tau_{02}^{-2}+g_4\tau_{01}^{-2}+g_5\tau_{01}^{-2}+g6=0, \tag{56}$$

where the coefficients are given as follows:

$$f_1=-m\alpha;\quad f_2=-2m;\quad f_3=n;\quad f_4=-n\alpha;$$

$$g_1=\frac{12m\beta}{\alpha};\quad g_2=-\frac{n\beta}{\alpha};\quad g_3=n\beta;\quad g_4=m\beta; \tag{57}$$

$$g_5=\frac{n^2\beta^2}{\alpha};\quad g_6=-\left[\gamma^2+\frac{1}{\omega_0^2\omega_p^4}\left[\frac{d^6F_{QQ}(k,t)}{dt^6}\right]_{t=0}\right];$$

$$\beta=\left(\gamma^2-\frac{\xi^2\rho e^2}{S_{QQ}(k)}\right);\quad \alpha=\frac{\xi^2\rho e^2}{S_{QQ}(k)}.$$

Expressions (55) and (56) can be solved for the relaxation times yielding for τ_{01}:

$$\tau_{01}^{-1}=\frac{-(f_1+f_2\tau_{02}^{-2})-\sqrt{(f_1+f_2\tau_{02}^{-2})^2-4f_3f_4\tau_{02}^{-2}}}{2f_3\tau_{02}^{-1}}. \tag{58}$$

The relaxation time τ_{02} can now be obtained from the following eight-degree algebraic equation

$$H_1\tau_{02}^{-8}+H_2\tau_{02}^{-6}+H_3\tau_{02}^{-4}+H_4\tau_{02}^{-2}+H_5=0. \tag{59}$$

From the eight roots of this equation we must select the one with physical meaning for τ_{02}. It has been found that the value of τ_{02} is of the order of ten [25] (frequencies are normalized to ω_p). We have calculated the root around this value numerically.

The coefficients of the above equation are given by

$$\begin{aligned}
H_1&=4f_3^2G_1G_2,\\
H_2&=4G_1[-f_3f_4G_3-4f_3^2G_5]G_5,\\
H_3&=-4f_1f_3^2g_3G_3-4f_1f_3f_4G_1G_7-4g_6f_3^2[f_1G_1+f_2G_3]\\
&\quad+4f_2f_3G_6G_5+8f_3^2G_8G_5,\\
H_4&=-8f_3f_4G_3G_6+2f_1f_3G_5G_6+4f_1f_3f_4G_7G_3\\
&\quad-4f_1f_3^2g_6G_3+4f_2f_3f_4G_7G_6-4f_2f_3^2g_6G_6\\
&\quad+8f_3^2f_4g_6G_7-4f_3^2[f_4G_7+f_3^2g_6^2],\\
H_5&=-4f_1f_3^2g_6G_6,
\end{aligned} \tag{60}$$

with

$$\begin{aligned}
&G_1=f_2g_2-f_3g_1;\quad G_2=f_4g_1-f_2g_3;\\
&G_3=f_1g_2+f_2g_4+f_2g_5;\quad G_4=f_2g_6+f_1g_3;\\
&G_5=f_4g_2-f_3g_3;\quad G_6=f_1g_4+f_1g_5;\\
&G_7=g_4+g_5;\quad G_8=f_3g_6-f_4g_4-f_4g_5.
\end{aligned} \tag{61}$$

We have assumed that the discriminant of Eq. (41) is less than zero. To solve this equation it is necessary to take into account an explicit expression for the sixth-order momentum. It is possible to obtain this expression from the distribution function theory, appearing in terms of the three-particle distribution function [26]. Therefore, we follow an alternative procedure to solve Eqs. (55) and (56) for τ_{01} and τ_{02}. We propose an expression for the sixth-order momentum, that corresponds to an interpolation of the well-known expressions valid for the extreme limits $ka \gg 1$ and $ka \ll 1$. These correspond to the so-called free particle and hydrodynamic limits, respectively.

In the hydrodynamic limit, we may consider the following relationship between the memory function and the static conductivity σ [8]:

$$\lim_{k\rightarrow 0}\lim_{\omega\rightarrow 0}\frac{\tilde{R}_{55}(k,z)}{\langle J_k^Q J_{-k}^Q\rangle}=\frac{\omega_p^2}{4\pi\sigma}. \tag{62}$$

Assuming an exponential memory and using the above relation, one can obtain the expression for the relaxation time τ_{02} in the hydrodynamic limit as

$$\tau_{02}^{-1}(H)=4\pi\sigma^0\left[\gamma^2-\frac{\xi^2\rho e^2}{S_{QQ}(k)}\right], \tag{63}$$

where we have the relations $\sigma=\sigma^0\omega_p$, $\gamma=\omega_{1l}/\omega_p$, and $\xi=\omega_0/\omega_p$.

Equation (63) can be generalized to be valid for small k, namely, the generalized hydrodynamics regime. In this case one has the relation

$$\tau_{02}^{-1}(GH)=4\pi\sigma_l^0(k)\frac{[\gamma^2-\xi^2\rho e^2/S_{QQ}(k)]}{\xi^2\rho e^2/S_{QQ}(k)}, \tag{64}$$

where $\sigma_l^0(k)=\lim_{\omega\rightarrow 0}\sigma_l(k,\omega)/\omega_p$. By substituting Eq. (64) in Eq. (56), one obtains

$$\begin{aligned}\left\{\frac{1}{\omega_0^2\omega_p^4}\left[\frac{d^6F_{QQ}(k,t)}{dt^6}\right]_{t=0}\right\}_{HG} &=\frac{\beta}{\alpha}\{12m\tau_{01}^{-1}(GH)\tau_{02}^{-2}(GH)-n\tau_{01}^{-2}(GH)\tau_{02}^{-2}(GH)\\ &\quad+n^2\beta\tau_{01}^{-2}(GH)\}+\beta\{n\tau_{02}^{-2}(GH)+m\tau_{01}^{-2}(GH)\}-\gamma^4.\end{aligned} \tag{65}$$

The relaxation time $\tau_{01}(GH)$, according to Eq. (58), is related with $\tau_{02}(GH)$ through

$$\tau_{01}^{-1}(GH)=\frac{-[f_1+f_2\tau_{02}^{-2}(GH)]-\sqrt{[f_1+f_2\tau_{02}^{-2}(GH)]^2-4f_3f_4\tau_{02}^{-2}(GH)}}{2f_3\tau_{02}^{-1}(GH)}. \tag{66}$$

On the other hand, in the free particle limit, there are some proposed expressions for the relaxation time. One of the most commonly used is due to Lovesey [27], where τ is written in terms of a density correlation, and is a suitable approximation for the description of neutral fluids with exponential type memory. Assuming a generalization for charged fluids, we propose for a symmetric molten salt system the following expression for the $\tau_{02}(F)$ relaxation time,

$$\tau_{02}^{-1}(F)=\frac{2}{\sqrt{\pi}}\sqrt{\gamma^2-\frac{\xi^2\rho e^2}{S_{QQ}(k)}}. \tag{67}$$

From Eq. (56) we can obtain an expression analogous to Eq. (65) for the sixth-order momentum. Here we must replace GH by F to indicate the free particle regime. For the relaxation time $\tau_{01}(F)$, we obtain an expression similar to Eq. (66), where HG must be changed by F. Hence, by interpolating the behavior of both regimes, we propose the following expression for the sixth-order frequency momentum:

$$\begin{aligned}\frac{1}{\omega_0^2\omega_p^4}\left[\frac{d^6F_{QQ}(k,t)}{dt^6}\right]_{t=0} &=\left\{\frac{1}{\omega_0^2\omega_p^4}\left[\frac{d^6F_{QQ}(k,t)}{dt^6}\right]_{t=0}\right\}_F\\ &\quad+\left(\frac{(k_0a)^2}{(k_0a)^2+(ka)^2}\right)\\ &\quad\times\left[\left\{\frac{1}{\omega_0^2\omega_p^4}\left[\frac{d^6F_{QQ}(k,t)}{dt^6}\right]_{t=0}\right\}_{HG}\right.\\ &\quad\left.-\left\{\frac{1}{\omega_0^2\omega_p^4}\left[\frac{d^6F_{QQ}(k,t)}{dt^6}\right]_{t=0}\right\}_F\right].\end{aligned} \tag{68}$$

We use this expression to calculate the dynamic structure factor. We expect that this approximation may improve our description of charge correlations, for frequency values in the vicinities of both the hydrodynamic and the free particle limits. The dynamical structure factor $S_{QQ}(k,\omega)$ can now be written in the form

$$\frac{\pi S_{QQ}(k,\omega)}{S_{QQ}(k)}=\frac{\omega_p^{-1}\{x^2\alpha\beta(n\tau_{02}^{-1}+m\tau_{01}^{-1})+\alpha\beta\tau_{01}^{-1}\tau_{02}^{-1}(m\tau_{02}^{-1}+n\tau_{01}^{-1})\}}{x^8+S_1x^6+S_2x^4+S_3x^2+S_4}, \tag{69}$$

where

$$S_1=\tau_{01}^{-2}+\tau_{02}^{-2}-2\gamma^2,$$
$$S_2=\tau_{01}^{-2}\tau_{02}^{-2}+\gamma^4-2\alpha(\tau_{01}^{-2}+\tau_{02}^{-2})-2\beta(m\tau_{02}^{-2}+n\tau_{01}^{-2}),$$
$$S_3=-2\alpha\tau_{01}^{-2}\tau_{02}^{-2}+\alpha^2(\tau_{01}^{-2}+\tau_{02}^{-2})+\beta^2(m\tau_{02}^{-1}+n\tau_{01}^{-1})^2+2\alpha\beta(m\tau_{02}^{-2}+n\tau_{01}^{-2}),$$
$$S_4=\alpha^2\tau_{01}^{-2}\tau_{02}^{-2}. \tag{70}$$

Note that in the expression for the dynamical structure factor, the denominator is an eighth-degree polynomial, whereas, if we consider a second-order memory with a single relaxation time, the dynamic structure factor is given in terms of a fourth-degree polynomial [15].

IV. RESULTS AND COMMENTS

In this section, we discuss results for the charge-charge dynamic structure factor $S_{QQ}(k,\omega)$ obtained by expression (69). We compare these results with those obtained by the use of MSA and a single relaxation time second-order memory [15]. A discussion is also presented for the charge-charge correlation function $F_{QQ}(k,t)$ obtained from expression (40).

In the calculation of the structure factor (69), we have used the HNC approximation to obtain the pair-correlation function $g_{\alpha\beta}(r)$ of a soft-spheres system [24]. We wish to separate the effects resulting from the improved description of the static properties of the system using HNC (instead of MSA), from those associated with the second-order memory with one or two relaxation times. To do so, we discuss first the results obtained with HNC and an exponential second-order memory with one single relaxation time (EHNC1).

Figure 1 shows a comparison of our calculations EHNC1 for the dynamic structure factor with others reported for the same system [11], [15]. The figure displays results obtained by the fitting with an exponential memory (HE), MD calculations [11], and our results with one relaxation time memory and MSA (EMSA) [15]. As expected, the three approximations exhibit a good agreement with the MD results in the high-frequency regime, but the disagreement is evident in the low-frequency regime. Notice also that the HNC theory provides a better description than a mean-field approximation like MSA. This improvement is observed in the hydrodynamic limit as well as in the region of low frequencies. We remark that, except for intermediate frequencies (approximately $0.1\leqslant\omega/\omega_p\leqslant 0.6$) the results of EHNC1, are closer to those of MD, even though in our calculation of EMSA and EHNC1, we have used the same approximation for the second-order memory function.

We also have calculated the dynamic structure factor $S_{QQ}(k,\omega)$ [Eq. (69)], using HNC to obtain $g_{\alpha\beta}(r)$ and assuming an exponential second-order memory with two relaxation times [Eq. (24)]. These times are given by Eqs. (55) and (56). The sixth-order frequency momentum, was obtained by an interpolation (68) as explained above. These results are denoted by EHNC2 in Figs. 2 and 3. The approximations EHNC1 and EHNC2 are compared in Fig. 2. It is observed that the assumption of a second-order memory, depending on two relaxation times, only provides a slight improvement of the results compared with those obtained with a single relaxation time in the memory function. However, the dependence of the memory function on the amplitudes *n* and *m*, offers the possibility of a more detailed analysis about the influence of each one of the relaxation times on the dynamic behavior of the system. It has been shown that in the short-times regime, the Gaussian approximation for the second-order memory is better than an exponential one [25]. However, the Gaussian representation has a disadvantageous nonanalytical Fourier-Laplace transform. To facilitate a comparative analysis, we have chosen the simplified analytical expressions provided by the exponential approximation for the second-order memory with one or two relaxation times.

In Fig. 3 we illustrate the possibilities of a second-order memory function as given by the expression (24). We notice

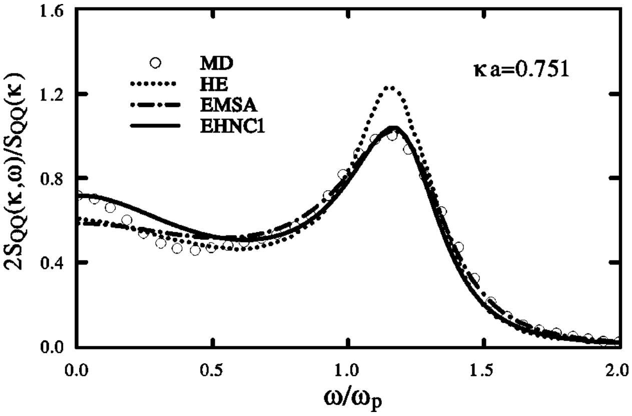

FIG. 1. The dimensionless dynamic structure factor $2S_{QQ}(k,\omega)/S_{QQ}(k)$ vs ω/ω_p. Comparison of the results of three different approximations with one relaxation time (see the text), and molecular dynamics.

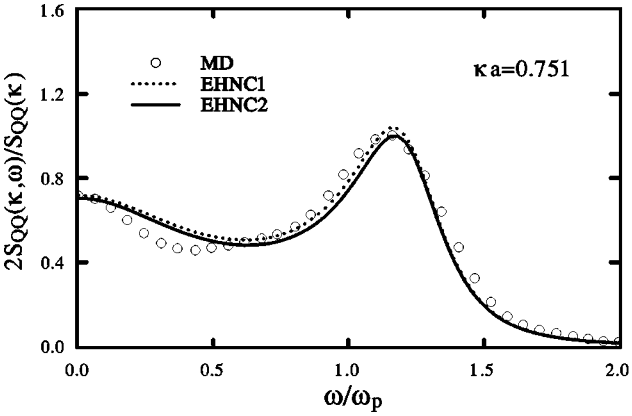

FIG. 2. $2S_{QQ}(k,\omega)/S_{QQ}(k)$ vs ω/ω_p, approximations with one (EHNC1) and two relaxation times (EHNC2), in comparison to the results of MD.

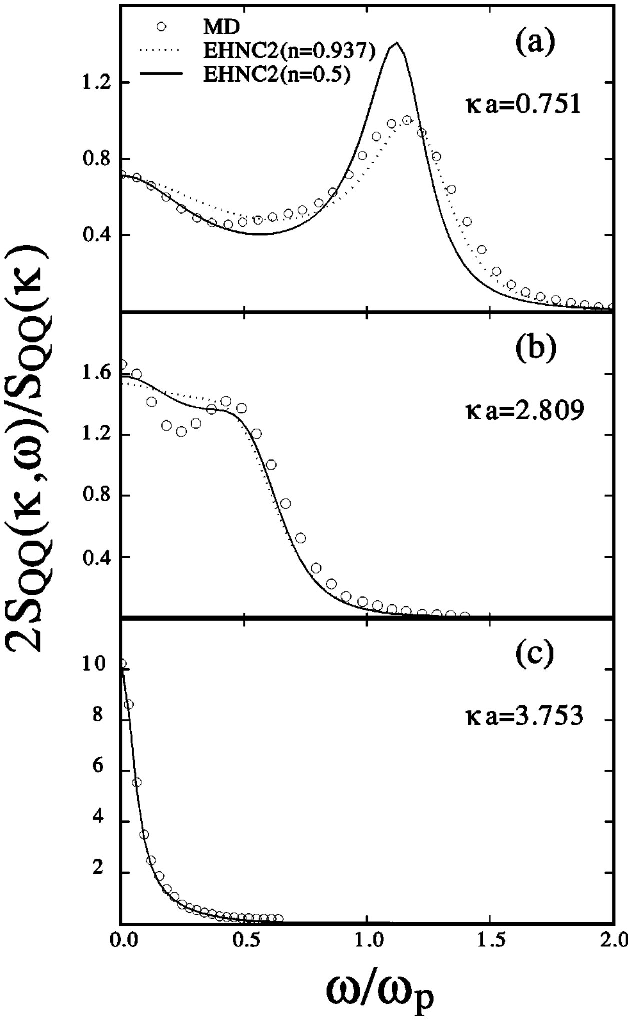

FIG. 3. $2S_{QQ}(k,\omega)/S_{QQ}(k)$ vs ω/ω_p. Effect of the change of the amplitude n of the second-order memory, and for three different values of the wave vector k, as indicated in (a), (b), and (c).

that it is possible ''to modulate'' the amplitudes n and m to obtain a better agreement with the MD results in the low-frequency region. However, we observe in Fig. 3(a) that the modulation of the amplitudes to produce a better agreement for low frequencies, also causes deviations from MD results at frequencies of the order and higher than the plasma frequency. Figure 3(b) reveals that the modulation of the amplitude n produces a slightly better agreement with MD calculations for the value $n=0.5$ than for $n=0.937$. One can see that our results EHNC2 fits better for this value of the wave vector $ka=2.809$, than for the value corresponding to Fig. 3(a), and that the effect of the modulation of the amplitude is less noticeable. This trend of our results to improve the general agreement for increasing values of ka, and to lessen the effect of the amplitude modulation, appears more clearly in Fig. 3(c); here one observes that the modulation of the amplitude n for $ka=3.753$, no longer affects the behavior of the structure factor.

Under the same considerations as in the previous figure we have also calculated the charge-charge fluctuations [Eq. (40)], this is displayed in Fig. 4. Here we present a comparison of our results EHNC2 for the charge-charge fluctuations with those obtained by the HE theory. It is interesting to analyze these results in relation to those depicted in Fig. 3(a).

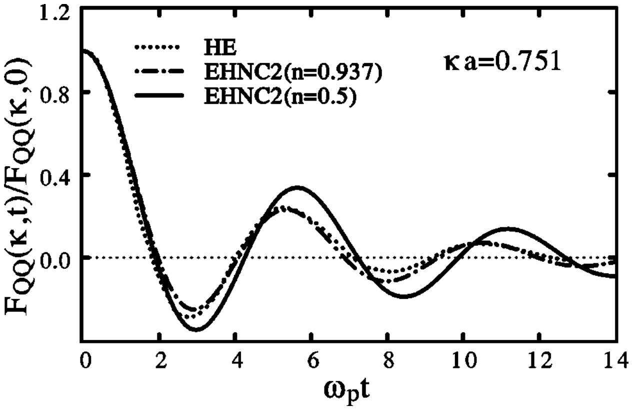

FIG. 4. Charge-charge correlation $F_{QQ}(k,t)/F_{QQ}(k,0)$ as a function of the dimensionless frequency $\omega_p t$. Effect of the changes of the amplitude n of the second-order memory. Comparison between results of the approximations EHNC2 and HE.

Notice that when the EHNC2 curve with $(n=0.5)$ for $S_{QQ}(k,\omega)$ shows a better agreement with the MD results, i.e., at low frequencies, the charge-charge correlation $F_{QQ}(k,t)$ increases. Figure 4, shows that when n increases, the amplitude of the correlations shows a clear tendency to decrease yielding a better agreement with the HE results. Another clear trend worthy of notice in these figures is the shift of the oscillation phase.

We conclude that in general the EHNC2 approximation for the exponential second-order memory with two relaxation times, together with the HNC approximation for the pair-correlation function, provide a better description of the dynamics of a symmetric molten salt than that obtained by fitting with an exponential memory HE, and the description with an exponential memory EMSA. The procedure we use in this paper can be further improved in the following two obvious aspects: (a) by using the hybrid approximation HNC/MSA for the pair-correlation function $g_{\alpha\beta}(r)$ instead of the pure HNC approximation [28], and (b) by calculating the sixth-order frequency momentum using the procedure proposed by de Gennes [26]. In this, the sixth-order momentum is evaluated in terms of the three-particle correlation function. In principle this procedure would provide a better approximation than the one provided by expression (68). These changes in the procedure followed in this paper would provide second-order corrections in the calculation of the dynamical properties of the charged fluid under study. On the other hand, a better approach of the second-order memory, for instance, assuming the memory proposed by Evelin *et al.* [25], would provide a first-order correction to the results reported in this paper. Finally, we recall that in our EHNC2 approximation, the roots of the fourth-degree polynomial, Eq. (36), are obtained numerically. These roots determine the relaxation times, and consequently the dynamical properties of the system. A more detailed analysis on the possibilities offered by the exponential memory with two relaxation times would be possible if an exact calculation of these roots is performed.

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[1] D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).
[2] Ph. A. Martin, Rev. Mod. Phys. **60**, 1075 (1988).
[3] D. L. Price and J. D. Copley, Phys. Rev. A **11**, 2124 (1975).
[4] K. M. Baloch and T. G. M. Van de Ben, J. Colloid Interface Sci. **50**, 2124 (1975).
[5] W. C. Kerr, J. Chem. Phys. **64**, 885 (1976).
[6] H. Mori, Prog. Theor. Phys. **33**, 423 (1965).
[7] R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Britton, B. W. Downs, and J. Downs (Wiley Interscience, New York, 1961), Vol. III, p. 135.
[8] P. V. Gianquinta, M. Parrinello, and M. P. Tosi, Physica **92A**, 185 (1978).
[9] M. C. Caccamo and G. Pizzimenti, Phys. Chem. Liq. **6**, 167 (1977).
[10] G. Jacucci, I. R. McDonald, and R. Rahman, Phys. Rev. A **13**, 1581 (1976).
[11] J. P. Hansen and I. R. McDonald, Phys. Rev. A **11**, 2111 (1975).
[12] J. D. Copley and A. Rahman, Phys. Rev. A **13**, 2276 (1976).
[13] M. Parrinello and M. P. Tosi, Riv. Nuovo Cimento **2**, 1 (1978).
[14] M. Dixon and M. J. Guillan, Philos. Mag. B **43**, 1099 (1981).
[15] J. E. Flores-Mena, M. A. Rodríguez, and J. L. Carrillo, Phys. Lett. A **236**, 563 (1997).
[16] H. L. Friedman, J. Chem. Phys. **73**, 3372 (1980).
[17] J. W. Perram, Mol. Phys. **30**, 1505 (1975).
[18] D. Henderson and W. R. Smith, J. Stat. Phys. **19**, 191 (1978).
[19] P. Shofield, Proc. Phys. Soc. **88**, 149 (1966).
[20] J. P. Hansen and I. R. McDonald, *The Theory of Simple Liquids*, 2nd ed. (Academic, London, 1990).
[21] *Dynamic Light Scattering*, edited by R. Pecora (Plenum, New York, 1985).
[22] M. C. Abramo, M. Parrinello, and M. P. Tosi, J. Nonmet. **2**, 67 (1973).
[23] P. Resibois and M. De Leener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1977).
[24] E. Lomba, Mol. Phys. **68**, 87 (1989).
[25] M. A. Evelin, I. R. McDonald, and K. Singer, Proc. R. Soc. London, Ser. A **357**, 37 (1977).
[26] P. G. de Gennes, Physica (Amsterdam) **25**, 825 (1959).
[27] S. W. Lovesey, J. Phys. C **4**, 3057 (1971).
[28] C. Regnaut and J. C. Ravey, J. Chem. Phys. **91**, 1211 (1989).